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TestAmerica, Inc.

Dayton Division

Standard Operating Procedure

Analyte or Suite: ICP Metals

Methodology: Inductively Coupled Plasma Atomic Emission

Reference: SW-846, 3rd Edition, July 1992, Method 6010A
EPA-600/4-79-020, Method 200.7
Standard Methods, 18th Edition, Method 3120 B

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1. INTRODUCTION AND SCOPE

1.1. General

Preservation: pH <2 using 1 part nitric acid to 2.5 parts water - approximately 2.5 mL.
Note: Use of dilute nitric for sample preservation in order to maintain compliance with DOT regulations.

Container: 500 cc plastic

Minimum sample volume: 100 mL

Holding Time: 6 months

Range of Test: Analyte Dependent

Nominal Reporting Limit: Division specific MDL- Analyte Dependent

Method No.(s) and References:
200.7, EPA 600/4-79-020, Revised March 1983
3120 B, Standard Methods, 18th Edition
6010A, SW-846, 3rd Edition

Regulatory Limits: Analyte Specific - see Drinking Water Regulations and RCRA Regulations.

1.2. Inductively coupled plasma atomic emission spectroscopy (ICP) determines elements including metals in solution. The method is applicable to a large number of metals and wastes. Sample digestions should be performed according to the guidelines and procedures established within the individual digestion SOPs. While drinking waters and filtered groundwater samples free of particulate matter, turbidity, and odor may be analyzed directly, EP/TCLP extracts, domestic waste, and industrial wastes require processing to solubilize suspended material. Sludges, sediments and other solid type samples may also be analyzed after proper pretreatment.

1.3. Some of the elements for which this SOP is applicable are listed in Table 1. A photomultiplier tube for each element is required on simultaneous instruments; only one photomuliplier tube is required on sequential instruments. Simultaneous instruments usually provide greater sample throughput, but are restricted in use to the elements that have a channel. Channels are selected at the time the instrument is purchased and consist of both the photomultiplier and slit. Sequential instruments are capable of analyzing a sample for any element for which a standard can be obtained within the wavelength range of 170 to 800 nm. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. Use of this SOP is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

2. SUMMARY OF METHOD

2.1. Definition of Terms

2.1.1. Detection Limit: Detection limits can be expressed as either an instrument or method parameter. The limiting factor of the former using acid water standards would be the signal to noise ratio and degree of scale expansion used; while the latter would be more affected by the sample matrix and preparation procedure used. The Scientific Apparatus Makers Association (SAMA) has approved the following definition for detection limit: that concentration of an element which would yield an absorbance equal to twice the standard deviation of a series of measurements of a solution, the concentration of which is distinctly detectable above, but close to blank absorbance measurement. (See SOP titled, Procedure for Detection Limit Studies, for additional information).

2.1.2. Reporting Limit (RL): The concentration of metals, equal to or above which, a value is reported to the client; otherwise "<" the reporting limit is reported. The reporting limit will be a specified multiple (e.g. 3) of the detection limit calculated as in 2.1.1 or as specified elsewhere in writing.

2.1.3. Dissolved Metals: Those constituents (metals) which will pass through a 0.45 u membrane filter.

2.1.4. Suspended Metals: Those constituents (metals) which are retained by a 0.45 u membrane filter.

2.1.5. Total Metals: The concentration of metals on an unfiltered sample following vigorous digestion or the sum of the concentrations of metals in both the dissolved and suspended fractions.

2.2. Atomic emission spectroscopy is a process in which the light emitted by excited atoms or ions is measured. This phenomenon occurs when sufficient thermal or electrical energy is available to excite a free atom or ion to an unstable energy state. Light is emitted when the atom or ion returns to the fixed or ground state. These wavelengths of light are specific for the elements present in a given sample.

2.3. This SOP describes the simultaneous, or sequential, multielemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry.

2.3.1. The Plasma

During plasma ignition, the gas stream is seeded with electrons from an external source. These electrons are accelerated in a torroidal path by the radio frequency electromagnetic field, and they collide with argon atoms to form more electrons and argon ions, which are in turn accelerated. This process continues

until the gas becomes highly ionized (a plasma), at which point the discharge is stable and self-sustaining as long as the RF field is applied. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tube(s).

2.3.1.1. Typical temperatures produced by the plasma are in the range of 6000 to 8000°K.

2.3.1.2. The high temperatures result in almost complete dissociation of molecules resulting in significant reduction in chemical interferences.

2.3.1.3. Two characteristics of plasmas are that they can conduct electricity and are affected by a magnetic field.

2.3.2. The Optical System

Multi-element analysis is accomplished with dispersive devices in two ways. Light from the plasma emission source is focused onto the entrance slit of the optical systems. After passing through the entrance slit, the light is dispersed by a diffraction grating. A narrow range of dispersed wavelengths pass through an exit slit(s) and falls onto a photomultiplier tube(s) (PMT) detector. The detector converts light energy to electrical current. The magnitude of the current is proportional to light intensity. The current is integrated over a predefined time period.

2.3.2.1. Simultaneous Instruments: When several exit slits and photomultiplier tube (PMT) detectors are used in the same spectrometer, the device is called a polychromator. Each exit slit in a polychromator is aligned to an atomic emission line for a specific element. The wavelengths of light measured by the detectors are determined by the position of the exit slits and photomultiplier tubes on the focal curve. All photomultiplier tubes are read simultaneously.

2.3.2.2. Sequential Instruments: When only one exit slit and photomultiplier tube (PMT) detector is used, the device is called a monochromator. Monochromators are used in multielement analyses by scanning rapidly from one emission line to another. This is done either by changing the angle of the diffraction grating by rotating it, or by moving the detector.

2.4. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in

background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in section 5 should also be recognized and appropriate corrections made.

2.5. For the best sensitivity, in order to determine elements with wavelengths below 190 nm, the photomultiplier tubes need to be in a vacuum or purged system. UV light below 190nm tends to be absorbed by oxygen, carbon dioxide, and water vapors, thereby reducing the amount of light passing from the entrance slit to the detector. Although argon is preferred, argon or nitrogen can be used to purge the system.

Table 1.

INSTRUMENT WAVELENGTHS AND STANDARD REPORTING LIMITS

Element	Wavelength	Reporting Limits mg/L	Reporting Limits mg/Kg
Aluminum	308.215	0.10	5.00
Antimony	206.833	0.10	5.00
Arsenic	193.696	0.10	5.00
Barium	493.409	0.020	1.00
Beryllium	313.042	0.005	0.25
Boron	249.678	0.050	2.50
Calcium	315.887	1.0	50.0
Cadmium	228.802	0.030	1.50
Chromium	267.716	0.040	2.00
Cobalt	228.616	0.020	1.00
Copper	324.754	0.020	1.00
Iron	259.940	0.100	5.00
Lead	220.353	0.080	4.00
Magnesium	279.079	1.0	50.0
Manganese	257.610	0.010	0.50
Molybdenum	202.030	0.020	1.00
Nickel	231.604	0.010	0.50
Potassium	766.491	1.0	50.0
Selenium	196.026	0.10	5.00
Silicon	288.158	1.0	50.0
Silver	328.068	0.040	2.00
Sodium	589.995	1.0	50.0
Strontium	421.552	0.010	0.50
Thallium	377.572	0.50	25.0
Tin	283.999	2.0	100
Titanium	334.941	0.020	1.00
Vanadium	292.402	0.050	2.50
Zinc	213.856	0.050	2.50

3. SAFETY

3.1. Each employee is directly responsible for complete awareness of all health hazards associated with every chemical that he/she uses. The employee must be aware of these hazards, and all associated protective wear and spill clean-up procedures PRIOR TO THE USE of any chemical. In all cases, both the applicable MSDS and supervisor or Safety Officer should be consulted. The employee should comply with all safety policies as presented in the TestAmerica Safety Manual. The bottle labels also provide important information that must be noted. If you have any questions, consult your supervisor or safety officer.

Personnel performing this procedure may be working with flammables, poisons, toxics, carcinogens, teratogens, mutagens, and biohazards. In particular, approved gloves, safety glasses, and labcoats must be worn, and solvents will be handled in ventilated hoods, in addition to other measures prescribed by the Division. It should be noted that samples must be handled with as much care as any of the materials used in this method due to the unknown nature of their composition.

3.2. The ICP spectrometer uses high power levels of radio frequency energy in the power supply and torch unit. This energy is potentially hazardous if allowed to escape. Safety devices and screening interlocks should not be bypassed or disconnected. The power supply of the instrument is capable of generating lethal voltages.

3.3. Never directly view the ICP torch without protective eyeware. Potentially hazardous ultraviolet radiation may be emitted from the torch. Ordinary safety glasses will, in general, provide sufficient protection, but additional side shields will insure a further margin of safety. The safety glasses will also provide mechanical protection for the eyes.

3.4. Gases commonly used with ICP instruments include argon and nitrogen. High pressure gas cylinders can be dangerous if mishandled.

3.4.1. Move gas cylinders with an approved handcart after insuring that the valve cap is secured.

3.4.2. Store gas cylinders in a vertical position only. Fasten securely to an immovable bulkhead or a permanent wall.

3.4.3. When gas cylinders are stored in confined areas, such as a small storage room, ventilation should be adequate to prevent toxic or explosive accumulations of gas.

3.4.4. Locate gas cylinders away from heat or ignition sources. Cylinders have a pressure-relief device which will release the contents of the cylinder if the temperature exceeds 52°C.

3.4.5. When the equipment is turned off at the end of the work day, close all gas cylinder valves tightly at the tank. Bleed the remainder of the line to the atmosphere before the exhaust fan is turned off. This is the preferred procedure. In some cases, it may not be possible to do this due to overnight runs and/or configuration of gas lines.

3.4.6. Perform periodic gas leak tests by applying a soap solution or Snoop Leak Detector to all joints and seals. Recommended frequency is once per week and/or whenever a tank is changed.

3.5. See manufacturer's instruction for proper installation of drain vessel.

4. REAGENTS AND MATERIALS

4.1. Apparatus

The following apparatus is recommended for performing this procedure. Equivalent items should only be used as a last resort or when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. When an equivalent is used in place of the recommended apparatus, this deviation does not have to be defined in the division specific appendix. However, it is important to report any item which results in an improvement to the corporate technical support team so that they can assist in the distribution of Best Developed Practice (BDP).

4.1.1. Inductively Coupled Argon Plasma Spectrophotometer is a Thermo Jarrell Ash Enviro 36 model with a 300 sample autosampler.

4.1.2. Argon gas supply: Welding grade or better.

4.1.3. Pipets: Macro (Oxford) and micro (Eppendorf) pipets with disposable tips.

Oxford pipet 1-5 mL / pipet tip
Oxford pipet 5-20 mL / pipet tip
Eppendorf pipet tips 1-250 uL and tips

4.1.4. Glassware: All glassware should be washed with detergent, rinsed with tap water, dilute nitric acid, and rinsed three times with deionized distilled water. The concentration of the nitric acid should be at least 10%. Standard Methods, 18th Edition recommends the use of 1 + 1 nitric, 1 + 1 hydrochloric, or aqua regia. See Metals Glassware Washing Procedure.

4.2. Reagents

The following reagents are required to perform this procedure. When instructions are given on how to prepare a specific volume

of a reagent, larger or smaller volumes can be prepared as needed so long as the final concentrations remain the same. Any other deviation from the reagents used in this SOP could be detrimental to the quality of the data produced. Such deviations would have to be approved by the corporate technical support team and documented in the division specific appendix. The identification of a reagent which can be purchased pre-prepared could be a significant improvement in Best Developed Practice (BDP). Such information should be communicated to the corporate technical support team so that they can assist in the distribution of BDP.

4.2.1. Deionized water: Prepare by passing water through a mixed bed of cation and anion exchange resins or an equivalent source. Use deionized water for the preparation of all reagents, calibration standards, and dilution water.

4.2.2. Nitric acid (concentrated): If metal impurities are found to be present, use a spectrograde acid.

HNO_3
NFPA diamond: health = 3, flammability = 0, reactivity = 3, contact = 4.

Strong oxidizer. Contact with other material may cause fire. Liquid and vapor cause severe burns. May be fatal if swallowed. Harmful if inhaled and may cause delayed lung injury. Keep from contact with clothing and other combustible materials. Do not get in eyes, on skin.

4.2.3. Nitric Acid (1:1): prepare a 1:1 dilution with deionized water by adding the concentrated acid to an equal volume of water.

4.2.4. Hydrochloric acid (concentrated): If metal impurities are found to be present, use a spectrograde acid.

HCl
NFPA diamond: health = 3, flammability = 0, reactivity = 2, contact = 3.

Poison! Danger! Causes severe burns. May be fatal if swallowed. Do not get in eyes, on skin, on clothing. Avoid breathing vapor. Keep in tightly closed container. Use with adequate ventilation. Wash thoroughly after handling.

4.2.5. Hydrochloric Acid (1:1): prepare a 1:1 dilution with deionized water by adding the concentrated acid to an equal volume of water.

NOTE: Acids used in the preparation of standards and for sample processing must be reagent grade or better.

4.2.6. Gases: Gases should be of high purity. Air may be supplied from a compressed air line, a laboratory compressor, or from a cylinder of compressed air. Air must be cleaned and dried

through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

4.2.7. Snoop Leak Detector: Supelco Catalogue no. 2-0434

4.3. Standards

The following standards are recommended for performing this procedure. The use of alternative standards will be allowed as long as they are of equal or greater quality and there is an associated improvement in efficiency, productivity, or cost. Such improvements should be communicated to the corporate technical support team so that they can assist in the distribution of Best Developed Practice (BDP). When instructions are given on how to prepare a specific volume of standard, larger or smaller volumes can be prepared as needed so long as the volumes used are properly documented. Any deviations from the recommended standards and the recommended concentrations of those standards must be approved by the corporate technical support team and documented in the division specific appendix.

4.3.1. Stock standard metal solutions: Commercially available stock standard solution are to be used. The stock solutions are purchased at concentrations of 1000 or 10,000 mg/L.

CAUTION: Many metals are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling stock solutions.

4.3.2. Mixed Calibration Standard Solutions

4.3.2.1. Either purchase mixed calibration standards or prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in a volumetric flask. Standard solutions and ICV solutions are prepared with 6% HNO_3 and 5% HCl. See preparations of Standards and Preparations of Initial Calibration Verification Solutions. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. The typical shelf life for working standards is one month. The higher the concentration of the elements in the mixed standard, the longer the shelf life. Refer to Appendix II for specific shelf life information.

Routine typical calibration standard combinations are listed in Table 2

NOTE 1: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of deionized water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

Table 2.

MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Sr, Sn, Tl
IV	Al, Ca, Cr, K, Na, and Ni
V	B, Mg, Sb, Tl and Ag (See note 1)

4.3.2.2. Premixed standards can frequently be purchased from vendors such as SPEX (SPEX standards are available from Fisher Scientific).

4.3.2.3. The concentration of each calibrating standard is calculated from the concentration of the stock solution.

A generic formula is based upon the proportion, C1V1 = C2V2

where:

C1 = Concentration 1 C2 = Concentration 2
V1 = Volume 1 V2 = Volume 2

Example: $\frac{1000 \text{ mg/L stock standard} \times 1 \text{ mL}}{100 \text{ mL final volume}} = 10 \text{ mg/L standard}$

4.3.3. Independent Calibration Verification Standards (ICVS). For each metal analyzed, it is necessary to obtain and analyze an ICVS following each calibration. The ICVS is a standard obtained from a second source different than that used for preparing the curve. Recommended source for ICVS and/or PE samples is APG Catalogue Nos. 7878 and 7879.

4.3.4. Interference Check Standard

The interference check standard is purchased or prepared to

contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Recommended source is SPEX available through Fisher Scientific.

The SPEX catalogue nos. are as follows:

Two solutions are utilized, 1) INT-A1, which contains high concentrations of interfering elements, specifically Al, Ca, Fe, and Mg and, 2) INT-B1, which contains lower levels of 12 elements different from INT-A1. Details regarding the use of these solutions are outlined in section 7.15.

4.4. Blanks

4.4.1. Two types of blanks are required for the analysis. The calibration blank or reagent blank is used in establishing the analytical curve. The reagent blank should contain the same amount of acid as the standards used for instrument calibration. The procedure blank is used to monitor for possible contamination resulting from varying amounts of the acids used in the sample preparation.

4.4.2. Dilution water should contain the same concentration as the standards and blank used for instrument calibration.

4.4.3. If the sample analysis solution has a different acid concentration from that of the calibrating standards or blank, but does not introduce a physical interference or affect the analytical result, the same calibration standards may be used.

5. INTERFERENCES

5.1. Spectral Interferences

Spectral interferences are caused by: (1) overlap of a spectral line from another element: (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength.

5.1.1. Background Correction

Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line. Table 3. lists background correction points for each element.

Table 3.

Background Correction Points

Element	Location
Aluminum	20
Antimony	-19
Arsenic	20
Barium	20
Beryllium	-19
Boron	-19
Calcium	20
Cadmium	20
Chromium	-19
Cobalt	-19
Copper	-19
Iron	-19
Lead	20
Magnesium	-19
Manganese	20
Molybdenum	-19
Nickel	20
Potassium	20
Selenium	20
Silicon	-19
Silver	-19
Sodium	20
Strontium	20
Thallium	20
Tin	20
Titanium	20
Vanadium	-19
Zinc	20

5.1.1.1. Simple background shift is a shift in background intensity constant over a given range on either side of the analyte line either up or down. A single point correction could be applied.

5.1.1.2. Sloping background shift or wing overlap is a shift in background intensity not constant over a given range on either side of the analyte line. A two point correction could be applied.

5.1.1.3. Complex background shift is a shift in background intensity that varies significantly on either side of the analyte line.

5.1.1.4. Generally, methods for background correction use spectral scans or shifts that permit measurements at one or more position beyond the profile of the analyte line. This is called

off peak correction. The information obtained from measurements beyond the profile of the analyte line is used to subtract a background signal from the signal measured at the peak of the analyte line.

5.1.1.5. On a simultaneous instrument, the photomultiplier tubes are directly behind and in line with each element exit slit. A spectrum shifter is used to shift the light path to the right or left. Each correction point increases the analytical time 100%. Therefore, it is necessary to determine the common correction points for the elements of interest. Usually three or four common correction points can be determined for all the elements combined. The study should be performed on a variety of matrices and background correction points applicable to the various matrices should be chosen for routine analyses. The number of background correction points should be limited to three or four points.

5.1.2. Interelement Correction

Direct spectral overlap can be compensated for using this technique. Use of the IEC technique requires that the sample be analyzed for each interfering element suspected to be in the sample.

It sometimes becomes necessary to apply additional correction factors to the normal background correction. This occurs when elements in the sample produce a signal near the analyte wavelength that is being looked for. If correction factors are not used to correct for this a excessively high or low sample result will occur.

5.1.2.1. Inter-element correction factors can be estimated by calibrating the instrument and running high level single element standards to determine what effect they have on other elements.

The correction factors can be calculated as follows.

$$\text{IEC (k)} = \frac{\text{Apparent Concentration of analyte}}{\text{Known Concentration of interferent}}$$

5.1.2.2. Single Element ICP standards are required to perform inter-element correcting as AA standards are not pure enough. The known concentration of interferent should be greater than what is expected in the samples. In all samples, interferent results should be less than the concentration at which the IEC's were evaluated.

5.2. Physical Interferences.

Physical Interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and

surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Also, it has been reported that better control of the argon flow rate improves instrument performance: this is accomplished with the use of mass flow controllers.

5.3. Chemical Interferences

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

6. ANALYTICAL PROCEDURES

6.1. Preservation and Handling

When pre-preserved sample containers have been used for sample collection, it is the responsibility of the analyst to verify adequacy of preservation at the time the actual analysis is initiated.

6.1.1. All metals samples (except Cr VI) must be acidified to a pH <2 with nitric acid upon collection. When nitric acid preserved containers are shipped to the client, use 2.5 mL of 1 part nitric to 2.5 parts water. Metals analyses must be conducted within six months.

6.1.2. For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption, thus the collection and treatment of the sample prior to analysis requires particular attention. The quality control program should document through the use of spiked samples, reagent and sample blanks, that cleaning procedures are adequate. Care should be taken to verify the fact that the containers in which acid digested samples, blanks, and standards are packaged do not contribute contaminants. Before collection of the sample

a decision must be made as to the type of data desired, i.e., dissolved, suspended, or total.

6.1.3. For the determination of dissolved constituents the sample must be filtered through a 0.45 u membrane filter as soon as practical after collection. A glass fiber pre-filter may be used in combination with the 0.45 u membrane filter. Glass or plastic filtering apparatus using membrane filters are recommended to avoid possible contamination. The filtering apparatus should be acid washed prior to use and in between samples. Use the first 50-100 mL of filtered sample to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 HNO_3 to a pH of <2. Normally, 2-3 mL of (1:1) acid per liter should be sufficient to preserve the sample. Analyses performed on a sample so treated shall be reported as "dissolved" concentration.

6.2. Daily Analytical Sequence

6.2.1. Calibration Curve: two point daily (the blank is one point).

Re-analyze calibration standards for all analytes. Acceptance criteria is a recovery of +/- 5% true value.

6.2.2. Reagent Blank (RB): must be less than the reporting limit or within statistically established limits, whichever is lower. It needs to be run at the beginning, end and every ten samples.

6.2.3. Initial Calibration Verification Standard (ICV 1 and ICV 2): ICV must be analyzed after every calibration curve is run. Acceptance criteria is a recovery of +/- 10% of the true value.

6.2.4. Reporting Limit Verification Standard (RLV 1, RLV 2): the advisory control limits are +/- 30% of the true value.

6.2.5. Spectral Interference Checks (SIC 1, SIC 2, and SIC 3): the control limits for the interfering elements are +/- 10% of the true value. The control limits for the affected elements must be +/- one reporting limit of zero. The warning limits are +/- 1/2 reporting limit from zero. Consistent results in the warning limits need investigation.

6.2.6. Reagent Blank (RB): another RB is run at this point to guarantee that there is no carryover from the SICs.

6.2.7. Samples 1-10. This does include Method Blanks (MB), Laboratory Control Standards (LCS), and other QC including Matrix Spikes and Matrix Spike Duplicates (MS, MSD). Rinse times must be a minimum of one minute to prevent carry over.

6.2.8. Continuing Calibration Blank (CCB): see Reagent Blank.

6.2.9. Continuing Calibration Verifications (CCV): ICV is run every ten samples and has control limits of +/- 10% of the true

value.

6.2.10. If additional samples are to be analyzed, return to Section 6.2.7.

6.2.11. Always end the sequence with a SIC, RB and CCV.

If the instrument does not stay in control between CCVs, increase the frequency of CCBs/CCVs to 1 per 5 samples or add additional rinses after difficult samples.

The data should be kept on file for future reference.

6.3. Instrument Calibration

6.3.1. Operating conditions: The analyst should follow the instructions provided by the instrument's manufacturer for operation. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range to be valid. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results in a fashion that is easily retrievable for review and inspection.

6.3.2. After calibration, reanalyzed the calibration standards. For all analytes. Acceptance criteria is a recovery of +/- 5% true value.

6.4. Sample Analysis

6.4.1. Set up the instrument with proper operating parameters established in 6.2. The instrument must be allowed to become thermally stable before beginning (usually 30 min prior to calibration).

6.4.2. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions.

6.5. Metals Sample Calculations

A general outline for metal calculations follows.

If a sample is aqueous and no dilution or concentration is required (a standard preparation of 50 mL to 50 mL or 50:50 was employed), then the reported value is that which the instrument generated.

6.5.1. Dilutions

In the case where a dilution is performed (for example, a sample dilution of 50 mL to 100 mL), the dilution factor must be

considered. For example:

The ICP has an instrument reading of 0.200 mg/L

The final concentration would be determined by the following equation.

$$\frac{0.200 \text{ mg/L} \times 100 \text{ mL (Final Volume)}}{50 \text{ mL (Initial Volume)}} = 0.400 \text{ mg/L}$$

Furthermore, a dilution may be made at the time of analysis. A dilution is performed on a sample if the concentration is found to be out of calibration range. The dilution factor is written next to the sample identification with a notation such as 1:10, for a 1 mL to 10 mL dilution made. In calculating, this dilution factor must also be included in the calculation, i.e.

$$0.400 \text{ mg/L} \times 10 = 4.00 \text{ mg/L}$$

6.5.2. Concentration

If a concentration is required (200:10) then the concentration factor must be accounted for in the calculations.

$$\frac{0.200 \text{ mg/L} \times 10 \text{ mL (Final Volume)}}{200 \text{ mL (Initial Volume)}} = 0.010 \text{ mg/L}$$

6.5.3. Solids

For a solid, the preparation will be a specific weight (g) of sample to volume (mL). The value read by the instrument is first divided by the weight of the sample, then multiplied by the final volume. For example, if a preparation of 0.2500 g to 100 mL was made and the instrument reading was 0.500 mg/L, then the final value would be calculated as follows:

$$\frac{0.500 \text{ mg/L} \times 100 \text{ mL (Final Volume)}}{0.2500 \text{ g (Initial Weight)}} = 200.0 \text{ mg/Kg}$$

Note: For the purpose of simplifying how to perform the calculation, conversion units which would cancel out have been excluded.

The units for a solid sample will be mg/Kg and depending upon how the sample was prepared (the initial sample weight being based on either Dry Wt., or Air Dry) the appropriate weight basis is used in the reported result, i.e.

200.0 mg/Kg	For an As Is sample weight
200.0 mg/Kg DW	For a Dry Weight Basis
200.0 mg/Kg AD	For an Air Dried Sample

When a sample is analyzed and the data generated is below the instrument reporting limit for an element, that reporting limit is used in all calculations. For example, zinc by ICP has a reporting limit of 0.020 mg/L. If the instrument reading for the sample is 0.010 mg/L then the calculation would be as follows:

$$\frac{0.020 \text{ mg/L (Reporting Limit)} \times 100 \text{ mL (Final V)}}{0.2500 \text{ g (Initial W)}} = <8.00 \text{mg/Kg}$$

Soils and sediments should be expressed on a dry weight basis, while waste materials are expressed on a wet weight basis.

Conversion of wet weight result to dry weight basis:

$$\frac{\text{Wet Weight Samples Result}}{\text{The decimal equivalent of the \% Total Solids}}$$

6.5.4. TCLP

For a TCLP (extraction) there are maximum contaminant levels. When reporting a less than value, the maximum contaminant level cannot be exceeded. Should the TCLP require a dilution (due to interference), care must be taken so the final result does not exceed the limits. If this situation is unavoidable, a notation must be made in the final report. Other samples, such as potables, must be reported in this same manner.

6.5.5. Punctuation, Capitalization, Significant Figures

Attention to punctuation, capitalization and significant figures are necessary when reporting results. Examples of these are presented below.

1.) A zero preceding the decimal is required in all instances.

2.) Commas are used when reporting numbers in the thousands or greater.

3.) Report units such as mg/Kg or mg/L with the K in Kg and L in being capitalized.

4.) The level of significance for reporting results are indicated in the method reporting limits table.

6.5.6. Accuracy

6.5.6.1. The calculation for accuracy is:

$$\text{Accuracy} = \frac{\text{(Spiked Sample)} - \text{(Original Sample)}}{\text{Spike Value}} \times (100)$$

6.5.7. Analytical Spikes

Analytical spikes are spikes that are done at the instrument

right before analysis occurs. Analytical spikes are done on dissolved and potable samples that are not digested. The volume of the spikes added does not significantly impact the results. The percent change in volume is only 5 %. Twenty mL of sample is used along with 1 mL spiking solution which is made up of separate solutions. For directions on how to make the spiking solution and its concentration see the section on Preparation of Spiking Solutions. The percent recovery calculation for undigested spikes is as follows:

$$\% \text{ RECOVERY} = \frac{\text{Spiked sample result - Sample result}}{\text{Expected spike concentration}} \times 100$$

6.5.8. Matrix Spike

Another type of analyte spike is the matrix spike. For this type of spike there is no dilution of the original sample. A sample was analyzed for Pb. The concentration for the sample was 0.560 mg/L. A 1.00 mg/L spike was added to another aliquot of the sample with the same volume as the original digestate and digested. The sample is poured up to the same final volume. The concentration of Pb for the Matrix spike was 1.24 mg/L. The percent recovery is calculated as follows:

$$\% \text{ Recovery} = \frac{1.24 \text{ mg/L} - 0.560}{1.00 \text{ mg/L}} \times 100 = 67 \%$$

For digested spikes with a weight of original sample the calculation is done as follows.

The instrument reading of Al in a soil sample with a weight of 1.4561 g was determined to be 2.50 mg/L. The sample was poured up to 100 mL final volume. Another aliquot of the soil with a weight of 1.8761 g was spiked with 2.00 mg/L of Al and also poured up to 100 mL final volume. The instrument reading for the spiked sample was 5.11 mg/L. The calculation of the percent recovery of the spike is as follows:

First, the spike amount for the MS needs to be calculated in mg/Kg.

$$\frac{(2.00 \text{ mg/L}) \times (100 \text{ mL})}{(1.8761 \text{ g})} = 106.6 \text{ mg/Kg}$$

To calculate the percent recovery, the following should be performed.

$$\frac{272.37 \text{ mg/Kg MS} - 171.69 \text{ mg/Kg original sample}}{106.6 \text{ mg/Kg spike conc}} \times 100 = 94.5\%$$

6.5.9. Precision

6.5.9.1. The calculation for Precision as Relative Percent Difference (RPD) is:

$$RPD = \frac{\text{(Larger Value - Smaller Value) X 100}}{\text{(Sum of the Values) / 2}}$$

Precision (RPD) must be less than 20%.

6.5.10. Other Calculations

Filters:

(conc. mg/L) X (volume L/filter) = mg/filter
(0.02 mg/L) X (0.050 L/filter) = 0.001 mg/filter
note: usual reporting = ug/filter

Dry Weight:

$$\frac{\text{(conc. mg/L) X (L)}}{\frac{\text{wet weight}}{\text{\% solids}}}$$

Silica:

(2.14) X (Silicon conc. mg/L) = _____mg/L

Potash (K_2O):

(1.205) X (Potassium conc. mg/L) = _____mg/L

Cation Exchange Capacity:

$$\frac{\text{(Na conc. mg/L) X (10)}}{\text{(weight used -g) X (Mol Wt. Na 23)}}$$

= _____ miliequilivants/ 100g

Lbs/ acre = (__ mg/Kg) X (2)

ug/L: (conc. mg/L) X 1000 = (conc. ug/L)

oz/gal: (conc. mg/L) X 0.00013 = (conc. oz/gal)

Relative Standard Deviation (RSD)

$$\% RSD = \frac{STD\ DEV}{MEAN} \times 100$$

Acceptance Criteria
-20 % for all results between the reporting limit and 2X the reporting limit except metals that have an inflated R.L. (Ca,Na,K,Mg,Sn,Si)
-10 % for all other results

6.5.11. Rounding Off

Round off by dropping digits that are not significant. If the digit 6, 7, 8, or 9 is dropped, increase preceding digit by one unit; if the digit 5 is dropped, round off preceding digit to the nearest even number: thus 2.25 becomes 2.2 and 2.35 becomes 2.4.

As a practical operating rule, round off the result of a calculation in which several numbers are multiplied or divided to as few significant figures as are present in the factor with the fewest significant figures. (SW-846, Method 1050B)

7. Quality Control

The following details the QC requirements which apply to this analysis. Each Quality Control Indicator (QCI) provides information pertaining to either instrument performance, method performance (including sample preparation), or individual sample performance. Our goal is to produce data of unquestionable quality. Always remember what purpose the QCI serves when evaluating QCI results. Guidelines can be provided, and are provided, but they cannot take the place of a logistical, common-sense evaluation of the complete data set.

7.1. Method Detection Limits and Reporting Limits

An MDL study, following the MDL SOP, must be done during initial method validation and then annually. If the analytical method is changed, an MDL study must be done again. Also, the calculated MDL must not exceed the reporting limit. The current nominal reporting limits are analyte dependent.

7.2. Method Validation Sample (MVS)

7.2.1. Definition and Use of MVS

The purpose of the MVS is to verify and demonstrate that the method and/or analyst is capable of generating precise and accurate analytical data. Method validation samples consist of four replicate aliquots of spiked deionized water prepared and analyzed in a manner identical to samples. The spike concentration should be at the mid range of the analysis. The samples should be prepared and analyzed in the same batch. They are used to validate new analyst and new instrument performance, and to validate changes in analytical equipment or techniques. MVS requirements are built into internal analyst certification protocols.

7.2.2. Frequency of MVS

Method validation must be repeated whenever a significant change in the method or instrumentation is made which could cause the previous MVS to become invalidated. Also, they will be routinely

analyzed as part of training and certification of analysts newly performing the analysis.

7.2.3. Criteria for MVS

The average percent recovery should pass the interim acceptance criteria applied to the MS/MSD, which is 80-120%, and the relative standard deviation should be within ±20%.

7.2.4. Corrective Action for MVS

If a problem is indicated, it must be identified and corrected, and if necessary, MVSs must be re-prepared and re-analyzed. If the problem involves only the instrument, the MVSs must be re-analyzed.

7.2.5. Documentation

Since the MVSs serve several purposes, results of the method validation should be filed either with individual analyst training records, method validation records, or with instrument validation records. How they are filed is dependent on the reason for the study being performed. An alternative would be to file the results jointly and cross reference other files as appropriate. In either case, the data must be retrievable.

7.3. Analyst Certification

Each analyst performing this method must successfully complete the requirements detailed in the certification SOP. Three performance samples, which are administered by the QA coordinator, one near the reporting limit, one near the middle of the curve, and one which exceeds the linear range of the curve, need to be analyzed.

7.4. Instrument Profile

7.4.1. Definition and Frequency

An instrument profile check needs to be performed at a minimum of once every day and should be performed whenever there is a significant change in room temperature. The ICP is very sensitive to changes in temperature. The daily profile is recorded in the "ICP Daily Profile Check" log book.

7.4.2. Criteria

The profile solution that is currently being used is a 0.5 mg/L Cu solution.

7.4.3. Corrective Action

Upon profile completion the peak position should be within +/- 0.10 to continue with analysis. If the peak position is incorrect then adjust the entry slit appropriately until the

position is +/- 0.10.

7.5. Calibration Curve

7.5.1. Definition and Use of Calibration Curve

The purpose of a calibration curve is to relate instrument response to sample concentration. It also provides a way of verifying that the instrument response, over a predetermined concentration range, can be predicted using a mathematical equation. If the responses were erratic, there would be no accurate way to relate response to concentration. A blank and a standard is used to calibrate the instrument.

The concentration for calibration standards varies. See Standard Preparation for details. The RSDs of the individual standards recommended that the RSD be less than 5.5 % for most elements except Ca, Mg, K, Na, and Tl which have higher RSDs on average. If the majority of elements have RSDs between 5 % and 10 % then this indicates a problem with the instrument and the problem should be corrected before continuing with the run.

7.5.2. Frequency of Preparing Calibration Curve

When a daily curve system is used, the curve should be re-prepared if during the analytical run a CCV fails and corrective action is unsuccessful.

7.5.3. Criteria for Calibration Curve

Refer to the section in the SOP detailing instrument calibration.

7.5.4. Corrective Action for Calibration Curve

Since the calibration curve is used for calculating results for all samples and quality control indicators, an analyte cannot be reported from a run in which the calibration curve did not meet the criteria listed in the SOP. Perform any corrective actions necessary, and re-analyze the curve, the samples, and the quality control indicators.

7.5.5. Documentation

Raw data associated with constructing a calibration curve should be retrievable and recorded as part of the analytical run.

7.6. Initial Calibration Verification Standard (ICVS)

7.6.1. Definition and Use of ICVS

The purpose of the ICVS is to verify that the standards used to make the curve were chemically pure, prepared properly, and that they have not degraded significantly since the time they were made. The ICVS should be obtained from a different source than

the one used to prepare the standards used to construct the curve. The concentration of the ICVS should be at the high point of the calibration curve. This standard does not go through sample preparation stages. ICVSs can be obtained from a variety of sources including, APG, USEPA, a different lot. If the concentration of the ICVS is not at the high point of the calibration curve, then it will be necessary to rerun the high standard from the calibration curve after running the ICVS. This conforms to the QC section of Method 6010 - SW-846, 3rd Edition, July 1992.

The ICVS is sometimes referred to as External Standard or Standard Reference Material (SRM).

7.6.2. Frequency of ICVS

Analyze an ICVS immediately following a calibration curve to verify the curve.

7.6.3. Criteria for ICVS

Acceptance range is +/- 10% of the true value.

7.6.4. Corrective Action for ICVS

If the criteria for the ICVS cannot be met, re-evaluate the calibration curve to verify that all criteria have been met. Verify the acceptability of the source used for preparing the ICVS. Evaluate the concentration of the ICVS compared to the linear range of the analysis and the reporting limit. The concentration of the ICVS should be within the mid to upper range of the calibration. If none of the above solves the problem, contact your supervisor before proceeding with the analysis.

If the ICV is out of control for an element that is being analyzed the calibration must be repeated and the ICV reanalyzed. Should elements not being evaluated have ICVs out of control, the instrument must be recalibrated if the IECs play a significant role in the data reduction of the element of interest.

7.6.5. Documentation

Record the percent recovery of the ICVS on the raw data printout or in the lab book.

7.7. Reagent Blank (RB) / Continuing Calibration Blank (CCB)

7.7.1. Definition and Use of Reagent Blank

The reagent blank is a deionized water blank that is subjected to the same conditions that a non-prepared sample undergoes. The reagent blank will determine if any contamination or any memory effects are occurring. Normally, a reagent blank is analyzed

every time a CCVS is analyzed.

The Reagent Blank is a deionized water sample that contains 5 % HCl and 6 % HNO_3. The acceptance criteria for the RB is that all results be less than the reporting limit for the various elements. If a RB is above the reporting limit for an element that is not being analyzed on the run it can be ignored. If a RB is above the reporting limit for an element that is being analyzed on the run then all samples bracketed by the RB must be repeated. If an acceptable RB can not be analyzed, the instrument must be recalibrated and the RB repeated.

7.7.2. Frequency of Reagent Blank

Analyze a minimum of one reagent blank at the beginning and one at the end of each analytical batch. Also, analyze a reagent blank after a minimum of every tenth sample.

7.7.3. Criteria for Reagent Blank

Acceptance criteria requires the reagent blank to be less than the reporting limit. In cases in which the instrument is set to zero with the reagent blank or the reagent blank is subtracted, then this criteria applies to reagent blanks run after the initial reagent blank. Extra caution should be utilized when the reagent blank is greater than half the value of the reporting limit. If positive reagents blanks are frequently encountered, SW-846, 3rd Edition, July 1992 states the guideline as being three standard deviation of the mean blank value.

7.7.4. Corrective Action for Reagent Blank

Since the instrument/calculation is zeroed to the reagent blank, a reagent blank after the tenth sample or at the end of the run having a concentration greater than the reporting limit would indicate a contamination problem or possibly instrument drift. Determine the cause of the high reagent blank value, correct the problem, and re-analyze the samples following the last in control reagent blank/CCVS pair.

An in control reagent blank and an out of control preparation blank would be an indication of a contamination source within the sample preparation procedure.

7.7.5. Documentation

Record the concentration of the reagent blank on the raw data or in the lab book. If the run did not require a preparation blank, enter the end of run reagent blank result into LABSYS2 into the blank entry.

7.8. Continuing Calibration Verification Standard (CCVS)

7.8.1. Definition and Use of CCVS

Run ICV as a CCV. ICVs are not control charted. Percent

recovery must be within 90 to 110 %. If the CCV is out of control then all the samples back to the last good CCV needs to be repeated for the elements that were out of control as well as any elements that may be effected by interelement correction of the elements that were out of control.

7.8.2. Frequency of CCVS

Analyze a minimum of one CCVS at the end of each analytical batch. Also, analyze a CCVS after every tenth sample.

7.8.3. Criteria for CCVS

Acceptance criteria requires the percent recovery to be within 90-110% of the true value.

If the analysis does not normally require an LCS to be analyzed, statistical control limits should be generated for the CCVS instead. After a data base of 20-30 points has been collected, calculate the mean expressed as percent recovery and the standard deviation (s).

Upper Control Limit (UCL) = mean + 3s
Upper Warning Limit (UWL) = mean + 2s
Lower Warning Limit (LWL) = mean - 2s
Lower Control Limit (LCL) = mean - 3s

The control limits and warning limits are updated yearly or whenever the process is changed. The data from the initial daily CCVS must be plotted on a control chart. The purpose of control charting is to obtain real-time trend analysis of method performance.

Note: A statistical control chart must be generated for either the CCVS or the LCS, but not for both, with a chart for LCS having preference over a chart for CCVS.

7.8.4. Corrective Action for CCVS

If the CCVS is out of control, determine the cause, correct the problem, and re-analyze the samples following the last in control reagent blank/CCVS pair. 7.8.5. Documentation

Record the percent recovery of the CCVS on the raw data or in the lab book.

Note: SW-846, 3rd Edition, July 1992 refers to the CCVS as the instrument check standard.

7.9. Preparation Blank (PB)

7.9.1. Definition and Use of PB

The preparation blank is a deionized water blank that is

subjected to the same conditions that a prepared sample undergoes. Preparation may include leaching, and/or digestion. The preparation blank is used to demonstrate method performance. A "clean" preparation blank demonstrates that the preparation procedure is free of contamination.

7.9.2. Frequency of PB

Analyze a minimum of one preparation blank per preparation batch. A batch shall contain twenty samples or less.

7.9.3. Criteria for PB

Acceptance criteria requires the procedure blank to be less than the reporting limit.

Procedure blanks are not routinely subtracted from the analytical results.

7.9.4. Corrective Action for PB

If a preparation blank shows a detection above the reporting limit for a parameter, then the concentration of the blank vs. the samples in the batch will need to be compared.

If the concentration of the blank is above the reporting limit and a sample is greater than 10x the level of the blank, the sample can be reported with a flag indicating method blank contamination.

If the concentration of the blank is above the reporting limit and a sample concentration is less than 10x the level in the blank, the sample will need to be re-prepared.

If positive values below the reporting limit are observed, they should be evaluated in relation to the sample(s) and extra care should be taken to avoid reporting false positives.

7.9.5. Documentation

Record the concentration of the preparation blank on the raw data or in the lab book.

Enter the preparation blank result into LABSYS2 in the blank entry. If the run did not require a preparation blank, enter the reagent blank result into LABSYS2 instead.

7.10. Lab Control Standard (LCS)

7.10.1. Definition and Use of the LCS

The Lab Control Standard is normally a high or mid standard that is subjected to the same conditions that a prepared sample undergoes. Preparation may include leaching, and/or digestion. The LCS analysis is designed to serve as a monitor of the

efficiency of the entire procedure including sample preparation.

The LCS is spiked at the lower end of the linear range. See Preparations of Spiking Solutions for exact concentrations.

7.10.2. Frequency of LCS

Analyze a minimum of one LCS per batch. A batch shall contain twenty samples or less.

7.10.3. Criteria of LCS

Interim acceptance criteria requires the LCS to be within 85-115% of the true value.

After a data base of 20-30 points has been collected, calculate the mean expressed as percent recovery and the standard deviation (s).

Upper Control Limit (UCL) = mean + 3s
Upper Warning Limit (UWL) = mean + 2s
Lower Warning Limit (LWL) = mean - 2s
Lower Control Limit (LCL) = mean - 3s

The control limits and warning limits are updated yearly or whenever the process is changed. The data must be plotted on a control chart. If the analysis does not normally require an LCS, then CCVS should be charted instead. The purpose of control charting is to obtain real-time trend analysis of method performance.

7.10.4. Corrective Action for LCS

The inability of the laboratory to successfully analyze the LCS indicates a problem potentially related to the sample preparation procedures. This is especially true if the CCVSs were all in control. If the control windows are exceeded, all sample results associated with the LCS are suspect and should be re-prepared and reanalyzed, after the cause of the problem has been determined and corrected. If reanalysis of the sample occurs outside holding times or if insufficient sample is available for reanalysis, the results must be flagged and the LCS reported to the client.

7.10.5. Documentation

Record the percent recovery on the raw data or in the lab book. Enter the percent recovery of the LCS into LABSYS2 in the LCS entry.

7.11. Matrix Spike / Matrix Spike Duplicate (MS/MSD)

7.11.1. Definition and Use of MS/MSD

The Matrix Spike / Matrix Spike Duplicate pair are two separate aliquots of sample which are spiked with known concentrations of analyte and subjected to the same conditions that a sample undergoes. The recommended spike concentration should be 20% of the top standard or equal the low or mid standard from a three point curve performed the day of the analysis. These data are generated to determine long-term precision and accuracy of the analytical method on various matrices. These data alone cannot be used to evaluate the precision and accuracy of individual samples except for the sample chosen for the MS/MSD analysis.

For the Matrix Spike/Matrix Spike Duplicate, if the concentration of an analyte in the client sample is > 4X the level of the spike then the spiking level is insignificant to the sample and skewed spike recoveries may result. In these cases, calculate the spike recovery and add the following flag "LS" next to the data. This flag will be entered into LABSYS QC fields to indicate that the spike level was insignificant to the level in the sample chosen for the MS/MSD. If an MS/MSD sample is diluted and the concentration of the spiked sample meets the above conditions then use the following flat "DL" next to the data. This flag will be entered into LABSYS QC fields to indicate that the MS/MSD was diluted out. For MS/MSD tabulation purposes, i.e. (control charting) place the same codes in the RPD recording area.

7.11.2. Frequency of MS/MSD

Analyze a minimum of one MS/MSD pair per every analytical batch per matrix; the two matrices monitored are water and soil. An analytical batch is twenty samples or less.

7.11.3. Criteria for MS/MSD

Advisory MS/MSD recovery limits are 75%-125% of the expected value. The relative percent difference is to be less than 20.

After a data base of 20-30 points of a given matrix, i.e. aqueous and soils, have been collected, calculate the mean expressed as percent recovery and the standard deviation (s).

Upper Control Limit (UCL) = mean + 3s
Upper Warning Limit (UWL) = mean + 2s
Lower Warning Limit (LWL) = mean - 2s
Lower Control Limit (LCL) = mean - 3s

The control limits and warning limits are updated yearly or whenever the process is changed. The data must either be tabulated or plotted on a control chart. At a minimum, statistical control and warning limits must be calculated

separately for aqueous and soil matrices. These are advisory limits.

7.11.4. Corrective Action for MS/MSD

No action is taken on out of control MS/MSD data alone to qualify an entire batch. Action taken must be weighed carefully since it may be difficult to determine if poor precision and/or accuracy is a result of sample non-homogeneity/uniqueness, method defects, or laboratory technique. However, the data may be used in conjunction with other QC criteria to determine the need for qualifying the data. If the MS/MSD data is outside acceptance limits, check percent recovery for the LCS. If the LCS is in control, the procedure is in control and the data is acceptable. Potentially, a matrix problem exists. Additional steps may be taken to determine the extent of the matrix interference.

If the concentration of an analyte in the client sample is >4x the level of the spike, then the spiking level is insignificant to the sample and skewed spike recoveries may result. This is not unexpected.

If an MS/MSD sample is diluted and the concentration of the spiked sample meets the above conditions, then the spike may be diluted out. This also is not unexpected.

The following applies when the LCS is in control:

If the MS is in control and the MSD is out of control (or vice-versa), and the RPD is **not** acceptable, then the data is suspect. The analysis is suspect and an investigation should be made to determine an assignable cause for the unacceptable RPD. Documentation of an assignable cause is essential.

If the MS and MSD is out of control and the RPD is not acceptable, the scope of the implication must be evaluated. If the sample is part of a project, i.e., many samples from the same site/same client, the client should be contacted.

MS/MSD data out of control indicates potential matrix problems. The following procedure can be used to determine the scope of the interference for metals analyses which appear to have matrix problems:

Note: Use of the following procedure is not mandatory. It is up to each division to decide whether to incorporate the following procedure into their routine.

1) Perform a post digestion spike on the sample. If the post digestion spike falls within 85-115% of the true value, then the indication is that the matrix interference is limited in scope. If the post digestion spike does not fall within 85-115% two options exist.

a) If the original sample result was less than the

detection limits, and the post-digestion spike was less than 85%, it is possible that the result is skewed due to negative interference. If the original sample result was positive, and the post-digestion spike was greater than 115%, it is possible that the result is skewed due to positive interference . Verify/estimate scope of a negative or positive interference by analyzing a post digestion spike on a diluted sample aliquot. The original MS/MSD results must be reported in LABSYS and flagged, indicating that the recoveries were not within the acceptable range. If the above scenario was followed issue appropriate notification to the client in a cover letter or case narrative submitted with the final report.

b) Alternatively, re-analyze the sample using the method of standard additions (MSA).

7.11.5. Documentation

The data generated can be presented, if necessary, as a statement of precision and accuracy for a particular analysis on a given matrix. Record the percent recovery of the MS/MSD on the raw data or in the lab book. Enter the MS/MSD results in LABSYS2 into the MS/MSD entry.

Special Note: It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

Serial Dilution: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution should agree within ±10% of the original determination. If not, a chemical or physical interference effect should be suspected.

Post Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

7.12. TCLP Spiking Protocol

The Method of Standard Additions (MSA) will be required when:

7.12.1. The spike recovery of the contaminant is less than 50 % and the concentration is below the Maximum Contamination Level (MCL).

7.12.2. The Concentration measured in the TCLP was within +/- 20 % of the MCL.

7.12.3. Refer to Appendix for MSA spiking procedure.

7.13. Statistical Control Windows vs. Specifications

Within this section all of the QCIs listed have specified acceptance criteria, such as the LCS must be within ± 20%. In some cases, this specification is listed as "interim" and instructions are provided which require the generation of statistical control limits. If the generated statistical control limits are wider than the specification, the process should be questioned and carefully evaluated. If the process is not controlled, it is impossible to generate "tight" statistical windows. Occasionally, the process is in control but bias exists within the procedure. If this is the case, a statement should be amended to the SOP within the divisional specific appendix that explains the deviation.

7.14. Metals Specific QCI - Reporting Limit Verification Standard

7.14.1. Definition and Use of RLVS

The RLVS provide information regarding instrument performance at or near the reporting limit. The concentration of the RLVS should equal the reporting limit. If the reporting limit is close to the method detection limit, it may be necessary to raise the RLVS by a factor of 2-5.

Two RLVs are required to cover all the various reporting limits that are used with the elements. The RLVs are at or near the reporting limit. If the ICV is at or near the reporting limit for an element then a RLV does not need run for that element.

7.14.2. Frequency of RLVS

Analyze this standard after performing instrument calibration. In some cases, it may be possible to incorporate the RLVS standard into the calibration curve.

7.14.3. Criteria for RLVS

Advisory, acceptance criteria requires the percent recovery to be within ± 30% of the true value.

7.14.4. Documentation

Record the percent recovery on the raw data or in the lab book.

7.15. ICP Specific QCI - Interference Check Standard (ICS)

7.15.1. Definition and Use of SIC

The SIC standards are used to set or confirm that the correct

background correction intervals have been set for sequential ICP spectrometers and that the proper inter-element correction factors are set for simultaneous ICP spectrometers. The interference check standard is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors.

7.15.2. Frequency of SICs

The SIC standards should be analyzed at the beginning and end of each analytical run or twice during an eight hour shift - whichever is more frequent.

7.15.3. Criteria for SICs

The known interferent analyte concentrations must have a percent recovery of +/- 10%. Review the effects of the interferent analytes on all other elements to determine if the IECs are functioning correctly. All non-interfering analytes must have a value of +/- the elements reporting limit.

7.15.4. Corrective Action for SICs

If the SICs are not in control, recheck the IEC factors and rerun the SIC. If the SICs are still not in control, recheck the background correction points and rerun the SICs. An in control SIC is required for valid data to be reported.

7.15.5. Documentation

Record the percent recovery of the SIC standards on the raw data or in the lab book.

7.16. ICP Specific QCI - Linearity Range Analysis (LRA)

7.16.1. Definition and Use of the LRA

The linear range for each element is determined during instrument validation.

Linear Range Analysis is done at the maximum amount that would be accepted in a sample. Maximum Linear Range is determined by analyzing increasingly high amounts of metal until the Percent recovery is no longer within +/- 5% of the true value. The highest amount that produced acceptable results is considered the upper limit of the linear range. Table 4. lists linear range concentrations.

7.16.2. Frequency of LRA

A linear range check standard should be analyzed yearly or when instrument or standardization conditions have changed significantly.

7.16.3. Criteria for LRA

Acceptance criteria requires the percent recovery to be within 95-105% of the true value.

7.16.4. Corrective Action for LRA

If the LRA fails, check the calibration and verify the linear range by running multiple standards.

Table 4.

Linear Range Concentrations

Element	Linear Range
Aluminum	1000 ppm
Antimony	100 ppm
Arsenic	100 ppm
Barium	200 ppm
Beryllium	100 ppm
Boron	250 ppm
Calcium	1000 ppm
Cadmium	100 ppm
Chromium	250 ppm
Cobalt	100 ppm
Copper	200 ppm
Iron	500 ppm
Lead	200 ppm
Magnesium	1000 ppm
Manganese	100 ppm
Molybdenum	100 ppm
Nickel	100 ppm
Potassium	1000 ppm
Selenium	100 ppm
Silicon	200 ppm
Silver	5 ppm, 10 ppm with no HCl
Sodium	300 ppm
Strontium	100 ppm
Thallium	100 ppm
Tin	100 ppm
Titanium	20 ppm
Vanadium	100 ppm
Zinc	300 ppm

7.16.5. Documentation

The data should be kept on file for future reference.

8. REFERENCES

8.1. Methods for Chemical Analysis of Water and Wastes, USEPA, Environmental Monitoring and Support Laboratory EPA-600/4-79-020

8.2. Standard Methods For the Examination of Water and Wastewater, 18th Edition, APHA

8.3. Concepts, Instrumentation, and Techniques in Inductively Coupled Plasma Atomic Emission Spectrometry, Perkin Elmer.

8.4. Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition, Revised in September 1986.

8.5. Users Manuals for PE-40 and TJA 61E.

Appendix I

Instrument Maintenance

Preventive maintenance is an essential program that reduces instrument downtime and service calls. The time intervals between some maintenance procedures will vary according to the amount of use, the cleanliness of the lab and the nature of the samples being analyzed. Daily maintenance records will be kept in a daily maintenance log. Periodic maintenance will also be recorded in the daily log on the days that it is performed along with a description of the maintenance that was done. All other maintenance, including servicing and parts replacement, will be recorded in the instrument log book where a much more detailed account can be given. For an example of a page from the daily instrument log see the page following Appendix I.

The daily maintenance items are as follows (no particular order):

Item 1: The ICP waste container and drain system need to be checked. The waste container needs to be drained when it is 3/4 to 7/8 full. (Note: When the waste container is completely full it is difficult to remove from underneath the table without spilling large amounts of waste.) After the waste container has been emptied it must be refilled with approximately 5 Liters of deionized or tap water. (Note: This is done to help maintain the back pressure in the mixing chamber.) The drain lines need to be tightly connected and end of the line must be completely submerged in the waste container.

Item 2: The autosampler waste container and drain system need to be checked. Leaks in the drain lines can cause severe damage to the autosampler and the sample racks if not detected early. The waste container does not need to be dumped until it is nearly full.

Item 3: The peristaltic pump tubing needs to be checked for flat spots, discolorization, clogging, and air leaks. The tubing should be changed when any of these occur.

Item 4: The argon tank and regulator need to be checked to see if they are set up correctly. The pressure leaving the regulator at the argon tank should be around 60 psi. If the tank does not contain enough argon to run the entire day change tank before starting. (Note: the torch could be damaged by a gradual decrease in pressure as this may allow the plasma to come into contact with the top torch.)

Item 5: The mixing chamber and the torch assemblies must be inspected prior to the ignition of the plasma. The torch needs to be checked for signs of melting or heat damage to the argon gas lines coming to the torch. The torch also needs checked for salt build up and clogging; clean if necessary. The torch alignment needs to be checked and adjusted if necessary. The more centered the torch is between the RF coils the easier it is to ignite the

plasma. After the ignition of the plasma the mixing chamber should be examined for particulate matter and large vapor droplets. If either of these is found, then the plasma is shut off and the mixing chamber should be removed and cleaned. If an uneven spray pattern occurs such as spurting or pulsing, check the nebulizer and sample lines for clogging or salt build up; clean if necessary. (Note: The cleaning procedures are listed under the periodic maintenance section.)

The periodic maintenance is as follows (no particular order):

Item 1: The cleaning of the torch assembly will need to be done on a as needed basis. The higher the salt content the more frequent the cleanings will need to be. To clean torch disassemble and place in soapy water in a ultrasonic bath for 20 minutes. The tip of the torch can be soaked in a 20 % nitric solution for 1 hour to clean it. If that does not work a stronger solution can be used such as Aqua Regia for a shorter time.

Item 2: The cleaning of the mixing chamber often needs to be done following a high number of oily samples. A oily film will build up on the inside and cause large beads or droplets to form. The mixing chamber can be cleaned by removing and washing with warm soapy water and rinsing with deionized water. The mixing chamber need not be completely dry before reinstalling in the instrument. (Note: A 1 % hydrofluoric solution is very effective in removing the oily film but will result in high silicon readings for a period after the cleaning.)

Item 3: The nebulizer may need cleaned occasionally when clogging or salt build up occurs. This is done by carefully removing nebulizer and soaking in 20 % nitric for 10 minutes in an ultrasonic bath. After it has finished soaking towel dry and replace. (Note: A cleaning wire can be used to unclog the nebulizer but is not recommended as it is easy to damage the nebulizer.)

Item 4: The filters on the back of the ICP need to be cleaned every several months. Before removing the filters first turn off the main power switch located on the back of the instrument. The two metal screens on the back of the chronometer can be pried off with a Flathead screwdriver and be cleaned with warm soapy water. They should be dried in a drying oven before being put back on the instrument. The filter on the back of the power source can be removed and cleaned with a vacuum cleaner.

Item 5: The autosampler needs to be cleaned whenever it becomes dirty. To clean the autosampler arms use a paper towel with a little methanol on it to remove dirt. After cleaning lubricate arms and make sure the autosampler is working properly.

Item 6: The coolant reservoir may need to be dumped and refilled when water becomes cloudy, dirty, or algal growth occurs. After

refilling with deionized water add 5 mL algicide to help keep algae from forming. (Note: If the coolant water is not changed when it needs to be then a build up may occur in the lines and cause the ICP to shut down due to low coolant flow.)

Item 7: Sample flow rate will need to be checked and adjusted after replacing a nebulizer or any time the nebulizer appears to be pulsing or flow appears to be reduced. The flow rate can be checked by placing probe in a 10 mL graduated cylinder filled with deionized water and measure the amount drawn over a three minute period. The draw rate should be between 1.5-2.0 mL per minute, but consistent. Each time the flow is checked it should be recorded in the daily instrument log.

Item 8: Power Tube will need to be changed about every 1 to 2 years depending on usage. The tube should be changed when there is no longer sufficient power to ignite the plasma. To change the tube remove the bottom two cover plates on the front of the ICP.(Total of 12 screws.) The top plate is loose and will fall off when screws are removed. The bottom plate is attached to the power supply unit. Pull out power supply unit and remove the ventilation system from the top of it. (2 Screws) Clean screen while unit is open. Ground top of power tube to case with a long handled screw driver. Remove the power tube by turning it counter clockwise about a 1/4 turn and lift out. Do the opposite to install the new power tube. Do steps in reverse order to reinstall the power supply unit.

Item 9. The "D" mirror located near the torch periodically needs cleaned. A small flashlight can be aimed at the mirror to examine for dust and/or corrosion. If corrosion is severe then the mirror should be replaced. To clean the mirror use lens paper making sure not to touch the mirror surface with your hands.

Item 10. Check rubber tubing that connects argon lines to plasma torch. Replace if cracked or brittle. Cracked tubing may result in difficulty lighting plasma.

ICP DAILY MAINTENANCE LOG

Date	Analyst	Additional Maintenance Performed

Appendix II

Premixed Multi-Element Standards and QC

The following is a list of premixed solutions used to make Standards and QC.

MIXSTD 1 Spex catalog # MIXSTD1-100 or
EM Science catalog # EP60101-1

Be	50 mg/L	Mn	100 mg/L
Cd	150 mg/L	Se	200 mg/L
Pb	500 mg/L	Zn	150 mg/L

MIXSTD 3 Spex catalog # MIXSTD3-100 or
EM Science catalog # EP60103-1

As	500 mg/L	Si	100 mg/L
Mo	100 mg/L		

MIXSTD 5 Spex Catalog # MIXSTD5-100 or
EM Science catalog # EP60105-1

Sb	200 mg/L	Ag	50 mg/L
B	100 mg/L	Tl	200 mg/L
Mg	1000 mg/L		

QC-7 Spex Catalog # QC-7-500 or
Ultra Scientific catalog # IQC-007

Al	100 mg/L	Si	50 mg/L
Ba	100 mg/L	Ag	100 mg/L
B	100 mg/L	Na	100 mg/L
K	1000 mg/L		

QC-21 Spex Catalog # QC-21-500

Sb	100 mg/L	Cu	100 mg/L	Mo	100 mg/L
As	100 mg/L	Fe	100 mg/L	Ni	100 mg/L
Be	100 mg/L	Pb	100 mg/L	Se	100 mg/L
Cd	100 mg/L	Li	100 mg/L	Tl	100 mg/L
Ca	100 mg/L	Sr	100 mg/L	Ti	100 mg/L
Cr	100 mg/L	Mg	100 mg/L	V	100 mg/L
Co	100 mg/L	Mn	100 mg/L	Zn	100 mg/L

Interference Check Standard 5 (INTER 5)
EM Science catalog # EP20075-1

Al	1200 mg/L	Mg	3000 mg/L
Ca	6000 mg/L	Na	1000 mg/L
Fe	5000 mg/L		

Alternate Metals III
Spex Catalog # MN-4-500

Ca	500 mg/L	K	100 mg/L
Na	500 mg/L	Mg	100 mg/L

Preparation of Standards

There are five separate calibration standards and one calibration blank in the calibration curve. The calibration standards are prepared from a combination of purchased solutions and 1000 ppm stock solutions. The calibration blank is made using deionized water and has a HNO_3 concentration of 6% and HCl concentration of 5%.

The purchased solutions are:
- MIXSTD 1
- MIXSTD 3
- MIXSTD 5

Note: See premixed standard page for exact elements and concentrations in each standard mix.

Standard Stock #2 (used in place of MIXSTD 2 due to cost)

Volume	Solution	Diluted with 6% HNO_3 to	Final Conc.
10 mL	10,000 mg/L Fe	100 mL	1000 mg/L Fe
10 mL	1000 mg/L Ba		100 mg/L Ba
10 mL	1000 mg/L Cu		100 mg/L Cu
10 mL	1000 mg/L Co		100 mg/L Co
10 mL	1000 mg/L V		100 mg/L V

or

Appropriate volumes of standards to equal proper concentrations

Standard 1

Volume	Solution	Diluted with 6% HNO_3, 5% HCl to	Final Conc.
20 uL	10,000 mg/L Si	200 mL	0.500 mg/L Be
2 mL	MIXSTD 1		1.50 mg/L Cd
			5.00 mg/L Pb
			1.00 mg/L Mn
			2.00 mg/L Se
			1.50 mg/L Zn
			1.00 mg/L Si

Standard 2

Volume	Solution	Diluted with 6% HNO_3, 5% HCl to	Final Conc.
1 mL	Std. Stock #2	100 mL	1.00 mg/L Ba
			1.00 mg/L Co
			1.00 mg/L Cu
			100. mg/L Fe
			1.00 mg/L V

Standard 3

Volume	Solution	Diluted with 6% HNO_3, 5% HCl to	Final Conc.
2 mL	MIXSTD 3	200 mL	5.00 mg/L As
1 mL	1,000 mg/L Sn		1.00 mg/L Mo
20 uL	10,000 mg/L Sr		1.00 mg/L Sr
20 uL	10,000 mg/L Ti		5.00 mg/L Sn
			1.00 mg/L Ti

Standard 4

Volume	Solution	Diluted with 6% HNO_3, 5% HCl to	Final Conc.
1 mL	10,000 mg/L K	250 mL	20.0 mg/L Al
2.5 mL	10,000 mg/L Ca		100. mg/L Ca
0.5 mL each	10,000 mg/L Al,Na		2.00 mg/L Cr
50 uL each	10,000 mg/L Cr,Ni		2.00 mg/L Ni
			40.0 mg/L K
			20.0 mg/L Na

Standard 5

Volume	Solution	Diluted with 6% HNO_3, 5% HCl to	Final Conc.
2 mL	MIXSTD 5	200 mL	2.00 mg/L Sb
			1.00 mg/L B
			10.0 mg/L Mg
			0.50 mg/L Ag
			2.00 mg/L Tl

Preparation of Initial Calibration Verifications

The ICVs are made from a combination of purchased solutions and 1000 ppm stock solutions.

The purchased solutions are:
- QC-7 - QC-21 - Alternate Metals III

Note: See premixed standard page for exact elements and concentrations in each standard mix.

ICV

Volume	Solution	Diluted with 6% HNO_3, 5% HCl to	Final Conc.
5 mL	QC-7	500 mL	For Conc. See ICV 1 Conc. Table
5 mL	QC-21		
0.5 mL	10000 mg/L Sn		
10 mL	Alt. Metals III		
225 uL	10000 mg/L Si		
2.5 mL	1000 mg/L Tl		

ICV Concentration Table

Element	Conc. (mg/L)
Aluminum	1.00
Antimony	1.00
Arsenic	1.00
Barium	1.00
Beryllium	1.00
Boron	1.00
Calcium	11.0
Cadmium	1.00
Chromium	1.00
Cobalt	1.00
Copper	1.00
Iron	1.00
Lead	1.00
Magnesium	3.0
Manganese	1.00
Molybdenum	1.00
Nickel	1.00
Potassium	12.0
Selenium	1.00
Silicon	5.0
Silver	1.00
Sodium	11.0
Strontium	1.00
Thallium	6.00
Tin	10.0
Titanium	1.00
Vanadium	1.00
Zinc	1.00

Preparation of Reporting Limit Verifications

There are two Reporting Limit Verifications that are needed to cover the various reporting limits that are used. The Reporting Limit Verifications are prepared from the ICV.

Reporting Limit Verification 1 (RLV 1)

Volume	Solution	Diluted with 6% HNO_3, 5% HCl to	Final Conc.
20 mL	ICV	200 mL	0.10 mg/L Al 0.10 mg/L Sb 0.10 mg/L As 0.10 mg/L Fe 0.10 mg/L Pb 0.10 mg/L Se 0.10 mg/L Sr 1.0 mg/L Sn 1.1 mg/L Ca 1.1 mg/L Na 1.2 mg/L K

Reporting Limit Verification 2 (RLV 2)

Volume	Solution	Diluted with 6% HNO_3, 5% HCl to	Final Conc.
4 mL	ICV	200 mL	0.020 mg/L Ba 0.020 mg/L Be 0.020 mg/L B 0.020 mg/L Cd 0.020 mg/L Cr 0.020 mg/L Co 0.020 mg/L Cu 0.020 mg/L Mn 0.020 mg/L Mo 0.020 mg/L Ni 0.020 mg/L Ag 0.020 mg/L Ti 0.020 mg/L V 0.020 mg/L Zn

Note: All other metals not listed have high enough RLVs to be covered by the ICVs.

Preparation of Spectral Interference Checks

There are three Spectral Interference Checks which are made entirely from 1000 ppm standard stocks. They are made in separate solutions so that they do not interfere with each other.

Spectral Interference Check 1 (SIC 1)

Volume	Solution	Diluted with 6% HNO_3, 5% HCl to	Final Conc.
1 mL	10000 mg/L Mo	200 mL	50 mg/L Mo

Spectral Interference Check 2 (SIC 2)

Volume	Solution	Diluted with 6% HNO_3, 5% HCl to	Final Conc.
0.2 mL	10000 mg/L Co	200 mL	10 mg/L Co
0.2 mL	10000 mg/L Cr		10 mg/L Cr
0.2 mL	10000 mg/L Cu		10 mg/L Cu
0.2 mL	10000 mg/L Mn		10 mg/L Mn
0.2 mL	10000 mg/L V		10 mg/L V

Spectral Interference Check 3 (SIC 3)

Volume	Solution	Diluted with 6% HNO_3, 5% HCl to	Final Conc.
600 uL	10000 mg/L Al	200 mL	30 mg/L Al
2 mL	10000 mg/L Fe		100 mg/L Fe
400 uL	10000 mg/L Ni		20 mg/L Ni

Preparation of Spiking Solutions

The spiking solutions consist of three purchased solutions and one made from 1000 ppm stocks.

The three purchased solutions are:
- QC-7, QC-21, Alternate Metals III, INTER 5

Note: See premixed standards page for exact elements and concentrations in each standard mix.

The Multi-Element Spiking Solution (M.E. Spike) prepared from 1000 ppm stocks is made by:

Volume	Conc.	Diluted to with 6% HNO_3
5 mL	10,000 ppm Si	500 mL
5 mL	10,000 ppm Sr	
5 mL	10,000 ppm Sn	

Digested Standards
For a Laboratory Control Standard and the Matrix Spike/ Matrix Spike Duplicate:

Volume	Conc.	Added to
0.5 mL	QC-7	50 mL D.I. or sample
0.5 mL	QC-21	
2.0 mL	Al. Metals III	
2.0 mL	M.E. Spike	

Note: For expected concentrations see the spike concentration table at the end of this section.

Undigested Spiking Solution
For an undigested instrument spike:

Volume	Conc.	Added to
0.10 mL	QC-7	20 mL of sample
0.10 mL	QC-21	
0.40 mL	INTER 5	
0.40 mL	M.E. Spike*	

* If Si, Sr, and Sn are not target metals, 0.40 mL of DI Water may be substituted.

Note: For expected concentrations see spike concentration table at the end of this section.

Spiking Solution Concentrations

Element	Digested LCS, MS, MSD mg/L	Undigested MS, MSD mg/L
Aluminum	1.00	23.3
Antimony	1.00	0.48
Arsenic	1.00	0.48
Barium	1.00	0.48
Beryllium	1.00	0.48
Boron	1.00	0.48
Calcium	21.0	115
Cadmium	1.00	0.48
Chromium	1.00	0.48
Cobalt	1.00	0.48
Copper	1.00	0.48
Iron	1.00	95.7
Lead	1.00	0.48
Magnesium	5.0	57.6
Manganese	1.00	0.48
Molybdenum	1.00	0.48
Nickel	1.00	0.48
Potassium	14.0	4.8
Selenium	1.00	0.48
Silicon	4.5	2.1
Silver	1.00	0.48
Sodium	21.0	19.5
Strontium	5.00	2.38
Thallium	1.00	0.48
Tin	4.0	1.9
Titanium	1.00	0.48
Vanadium	1.00	0.48
Zinc	1.00	0.48

Shelf Life of Solutions

1000 ppm Standards - whichever is the earlier date
- 1 year from date of opening
- expiration date on bottle from manufacturer

Stock solutions (50.0 mg/L) - 6 months from date of preparation

Working standards and ICVs - 1 month from date of preparation

Reporting Limit Verifications - 1 month from date of preparation

Spectral Interference Checks - 1 month from date of preparation

Spiking Solutions - 3 months from date of preparation if not purchased
- if Spiking Solution is purchased, 1 year from date of opening or expiration date on bottle, whichever is the earlier date.

Copper Profile Solution - No Expiration Date

TCLP Spiking Solutions - 1 month from date of preparation

DRINKING WATER APPENDIX - ICP

For the analysis of potable samples, all calibration, sample handling and quality control procedures in this SOP must be followed with the addition of the following potable-specific procedures.

1. Sample Turbidity Screen

Sample turbidity must be determined for every potable sample in accordance with the procedures in the Turbidity Screen SOP.

1.1. Criteria

Samples with turbidity $\geq$ 1.0 NTU must be digested in accordance with the appropriate digestion SOPs prior to analysis. Samples with turbidity < 1.0 NTU may be analyzed without digestion. If the sample reads < 1.0 NTU, but particulate matter is visible in the sample, then the sample must be digested prior to analysis.

2. Sample pH

The pH of each potable sample must be determined to be < 2 prior to analysis. If the sample is preserved at the laboratory, then the sample must be held a minimum of 16 hours after preservation before the pH is taken and analysis is performed.

3. Reporting Limit Check (RLC) Samples

A low level standard (RLC) with a concentration less than or equal to the Ohio EPA reporting limit is analyzed to validate the calibration at or near the reporting limit. If one of the calibration standards is at or below the OEPA minimum reporting level, then an RLC is not required.

3.1. Frequency And Criteria

The RLC is analyzed after each calibration. Acceptance criteria is +/- 30% of the true value.

3.2. Corrective Action

If the criteria cannot be met, re-evaluate the calibration curve and verify the acceptability of the source used for preparing the RLC. If necessary, repeat the calibration and reanalyze the RLC. All elements being analyzed must have an acceptable RLC for potable analysis.

4. Independent Calibration Verification Standards (ICVS)

Both a high and a low concentration ICVS from a source separate from that used for instrument calibration must be analyzed to verify instrument calibration. Concentrations for the low ICVS are listed in Appendix 2. The high ICVS is 5 times the concentration of the low ICVS.

4.1. Frequency And Criteria

The high and low ICVS must be analyzed at the beginning of the run, following calibration, and at the end of the run. Acceptance criteria is +/- 10% of the true value.

4.2. Corrective Action

If the acceptance criteria cannot be met after calibration, re-evaluate the calibration curve and verify the acceptability of the source used for preparing the ICVS. If necessary, repeat the calibration curve and reanalyze the ICVS. All elements being analyzed must have an acceptable ICVS for potable analysis.

If the final ICVS does not meet acceptance criteria, then no data bracketed by the last acceptable Calibration Check Verification Standard (CCVS) can be reported.

5. Duplicates

Samples must be analyzed in duplicate to verify replication of analysis.

5.1. Frequency And Criteria

Duplicates must be analyzed at a frequency of 10% of samples analyzed. Acceptance criteria is reproducibility of results within +/- 20% for analyte concentrations greater than the OEPA minimum reporting limits.

5.2. Corrective Action

Poor reproducibility of sample results is indicative of matrix interferences or a lack of sample homogeneity. The sample should be diluted and analysis repeated.

6. Matrix Spikes (MS)

Matrix spikes are representative sample aliquots which are spiked with known concentrations of analyte. Concentrations are listed in Appendix 2.

6.1. Frequency And Criteria

Matrix spikes are performed at a 10% frequency. Acceptance criteria is +/- 15% of the true value for samples with analyte hits and +/- 20% of true value for samples with no analytes detected.

6.2. Corrective Action

If the concentration of the analyte is more than 4 times that of the spike, then the spiking level is considered insignificant, and skewed recoveries may result. If the matrix spike sample must be diluted to be brought into calibration range, then the spike may be diluted out resulting in low recoveries. While no action is required based on matrix spike recovery alone, the data must be reviewed carefully in conjunction with the other quality control indicators (QCIs).

7. Calibration Standards

Reanalysis of the calibration standards as described in Section 6.2 of this SOP is not required for potable samples.

TCLP APPENDIX - ICP

For TCLP extract analysis, all calibration, sample handling and quality control procedures in this SOP must be followed with the addition of the following TCLP-specific procedures.

1. Extraction Blanks

A TCLP extraction blank must be analyzed periodically to ensure that the process is free of analyte contamination.

1.1. Frequency And Criteria

One extraction blank must be analyzed for every 20 extractions performed. The extraction blank must be less than the analytical reporting limit for each analyte of interest.

1.2. Corrective Action

For analyte detections in the blank which are above the reporting limit, the extraction and preparation process must be suspended and investigated to determine the cause of the contamination and to take corrective action. Any affected samples must be repeated.

2. Matrix Spike Samples

A matrix spike shall be performed periodically to assess analyte recovery in the matrix type. Matrix spikes are to be added after extract filtration and before sample preservation. Matrix spikes are not to be added prior to the extraction process. Spiking procedures are described in Sections 6 and 7 of this SOP.

2.1. Frequency And Criteria

Matrix spikes are performed at a frequency of one per 20 samples. Acceptance criteria will follow the guidelines in the analytical SOP. However, if the recovery does not exceed 50%, then the Method of Standard Additions (MSA) will be used to assess analyte concentration.

2.2. Corrective Action

If the concentration of the analyte is more than 4 times that of the spike, then the spiking level is considered insignificant, and skewed recoveries may result. If the matrix spike sample must be diluted to be brought into calibration range, then the spike may be diluted out resulting in low recoveries. All samples that are spiked properly and still have unacceptable spike recoveries must be analyzed using the method of standard additions (MSA).

3. Method of Standard Additions (MSA)

MSA requires preparing calibration standards in the sample matrix, rather than reagent water, and is used to assess any matrix effects on analyte recovery. MSA is required for any TCLP extract in which the matrix spike recoveries do not exceed 50%, or when the concentration of the contaminant is within +/- 20% of the appropriate regulatory level.

3.1. Procedure

MSA requires 4 identical aliquots of the sample, 3 of which are spiked with known amounts of standard. The fourth aliquot is the unknown. The first standard addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third standard additions should be prepared so that the concentrations are 100% and 150% of the expected sample concentration.

All 4 aliquots are maintained at the same final volume by adding reagent water or blank solution and may need dilution adjustment to maintain the signals in the linear range of the instrument technique. All four aliquots are then analyzed.

3.3. Calculation of MSA Results

Prepare a linear regression plot of instrument signals as the dependent variable (y axis) versus standard concentration of the additions as the independent variable (x axis). Solve the plot for the abscissa (x axis intercept), which is the concentration of the unknown (prior to taking into account any dilution factors).

Hardness Calculation Appendix

1. Introduction and Scope

The commonly accepted definition of hardness is the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate, in milligrams per liter. This method can be used to calculate hardness on drinking, ground, and wastewaters.

2. Summary of Method

To calculate the actual hardness concentration, calcium and magnesium are analyzed on the ICP by EPA 200.7. The calcium and magnesium results must each meet all the QC requirements that are described in the ICP SOP. Hardness, as mg equivalent $CaCO_3$/L, is calculated from those results.

3. Sample Preparation

For drinking water samples, digestion is not required so long as the turbidity screen results are less than 1 NTU. If the turbidity screen results are greater than 1 NTU and for all other samples a digestion as described in the ICP Digestion SOP is required.

4. Calculation and Reporting of Results

Hardness, mg equivalent $CaCO_3$/L, is calculated as follows:

Hardness = 2.497 [Ca, mg/L] + 4.118 [Mg, mg/L)

Results should be reported as "Hardness (calculated)". The standard reporting limit is <5 mg/L. The ICP is set up to automatically do the calculation. The hardness result is identified by the parameter "Ha" on the data. Both the calcium and magnesium results need to be reviewed closely. The hardness results will sometimes need to be calculated by hand if dilutions are required or if one of the two parameters is approaching the MDL in concentration.

5. References

Method 2340 B, Standard Methods For The Examination of Water and Wastewater, 18th Edition, 1995